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MARKET OUTLOOK FOR SULFUR  
RECOVERABLE FROM COAL

BY

WALTER H. VOSKUIL

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# MARKET OUTLOOK FOR SULFUR RECOVERABLE FROM COAL

By WALTER H. VOSKUIL

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## PART I. THE SULFUR MARKET PROBLEM

### NEED FOR NEW SOURCES OF SULFUR

Sulfur from the salt domes of the Texas and Louisiana Gulf coast has been so abundant and produced at such low cost that it has been almost the sole source of supply. But in 1950 it became evident that rapidly expanding uses for sulfur would soon create a demand larger

than this supply could meet, and it would be necessary to make a survey of other possible sources.

There is no world shortage of sulfur; the problem is one of economic production rather than supply. The low cost of sulfur produced from the salt domes by the Frasch process has made it uneconomical to work the higher-cost sources. Now the picture is changing, and the following additional sources of sulfur have been suggested: pyrite, sulfur dioxide smelter gas, sulfur dioxide in stack gases, hydrogen sulfide in coal carbonization plants, oil refineries and "sour" natural gas, coal "brasses" from high-sulfur coals, and gypsum.

### ECONOMIC CHANGES IN THE SUPPLY PATTERN

The change from native sulfur to other sources of sulfur means higher production costs. It will cost more to ship the sulfur-bearing ores to points of consumption, and it will cost more to convert the sulfur to the forms needed by industry.

Elemental sulfur is easily transported, which accounts in part for its wide distribution in the United States and abroad. Pyrite is also easily transported, but it contains in its pure form only about 58 percent of sulfur. Commercial pyrite contains only about 41-43 percent. Transportation costs would therefore limit the distribution of this ore from the mine locality. To offset high transportation costs, every effort will be made to develop sulfur ores as near to the market as possible.

Sulfur dioxide, in liquid form, can be shipped in tank cars, and this form of transportation may become very important in the future. Sulfuric acid, the most important form in which sulfur is used, is very difficult to transport and store, and it is therefore advantageous to manufacture sulfuric acid as near as possible to the consuming center.

The sources of sulfur will be somewhat dictated by the sulfur raw materials that are locally available. The sulfur industry will therefore evolve into a large number of widely scattered producing units that use many processes adapted to the raw material available and to the markets to be served.

In order to appraise the trend of the sulfur market, it is necessary to analyze the uses of sulfur in industry and to describe the geographic markets for sulfur.

#### SULFUR IN INDUSTRY

##### *Preparation*

Except for small quantities used in elemental form, sulfur is used in industry mainly as sulfuric acid or sulfite liquor. In preparing these compounds, sulfur is first burned to  $\text{SO}_2$ . Where S is the raw material used, the preparation of  $\text{SO}_2$  is relatively simple and the cost is low. Production of sulfur or sulfur dioxide from natural compounds, such as hydrogen sulfide ( $\text{H}_2\text{S}$ ), metallic sulfides (iron, copper, lead, and zinc), or gypsum, entails considerable additional cost, both in the preparation of the product and in the assembly of raw materials.

##### *Industrial Use*

Industrial distribution of sulfur by uses is shown statistically in table 1. Increase in sulfur consumption has not been due to new developments

TABLE 1. USES OF SULFUR\*  
(thousands of long tons)

Use	1935		1940		1945		1949	
	Tons	Percent	Tons	Percent	Tons	Percent	Tons	Percent
Chemicals .....	555	45.0	800	43.3	1605	54.1	1765	50.4
Fertilizers & Insecticides .....	239	19.4	410	22.2	600	20.5	740	21.2
Pulp & Paper .....	204	16.6	320	17.5	297	9.9	330	9.2
Explosives .....	42	3.4	74	3.8	90	2.9	98	2.9
Dyes & Coal Tar Products .....	39	3.1	51	2.7	75	2.6	94	2.8
Rubber .....	33	2.7	47	2.5	58	1.9	53	1.5
Paint & Varnish .....	48	3.8	54	3.0	94	3.3	210	6.1
Food Products .....	4	0.1	6	0.1	7	0.1	8	0.1
Misc. ....	68	5.9	86	4.9	135	4.7	202	5.8
Total .....	1232		1848		2961		3500	

\*Source: Minerals Yearbooks, Bureau of Mines.



but to expansion of existing uses. Four consumer groups — chemical manufacture, fertilizers and insecticides, pulp and paper, and paint and varnish — account for 87 percent of consumption. They accounted for an increase of 2,000,000 tons between 1935 and 1949.

A forecast of future requirements made by projecting the curve of past consumption into the future suggests steady increase in sulfur requirements. In addition we may also assume that chemical, fertilizer, paper, and paint requirements will maintain a growing demand that is going to exceed the maximum output capacity of the Gulf Coast sulfur domes.

#### *Supply and Exports*

An important factor in the supply-demand relationships of native sulfur has been the high rate of exports. In the 15-year period 1935-1949, an average of 26 percent of the native sulfur produced has been exported. The record is as follows:

#### SULFUR EXPORTS, 1935-1949

Annual Average in long tons

Production .....	3,175,238
Exports .....	816,900
Percent, exports of production .....	25.8

#### GEOGRAPHIC MARKETS FOR SULFUR

##### *Production and Shipments*

The principal markets for sulfur are the sulfuric acid plants, which are concentrated in the Atlantic seaboard states, in Illinois and Ohio, and in the southern states. The approximate distribution of sulfuric acid manufacture is shown in table 2, given in the Census of Manufactures, for 1947.

The sulfur market has been favored by two low-cost items—production by the Frasch process, and low-cost water transportation for a large portion of Gulf Coast sulfur destined to markets on the Atlantic seaboard and ports on the Mississippi River system.

The distribution of sulfur by coastwise shipments, by inland waterways, and by all-rail haul reflect the wide geographic usage of sulfur. Ninety-seven of the 120 Class I steam railways in the United States report sulfur shipments terminating on their lines. Sulfur shipments to the southeastern states enter the superphosphate manufacturing industry; those to the Middle Atlantic states are primarily for industrial production. Sulfur destined to New England, the Upper Lake states and the Pacific Northwest figures largely in paper manufacture. In the Upper Mississippi-Ohio Valley shipments, sulfur enters a diversified market in steel, petroleum refining, paint and rubber manufacture.

##### *Illinois and Adjacent Markets*

The sulfur markets in states of the Upper Mississippi and Ohio river valleys have one advantage in common—transportation by barge on the

TABLE 2. PRODUCTION AND SHIPMENTS OF SULFURIC ACID<sup>1</sup> (100% H<sub>2</sub>SO<sub>4</sub>),  
BY DIVISIONS AND STATES: 1947\*

Division and state	Number of producing establishments	Short tons	Value f.o.b. plant (thousands)	Total production (short tons)
United States <sup>2</sup> .....	177	6,824,756	\$89,129	10,780,166
New England <sup>3</sup> .....	5	102,156	1,808	183,151
Middle Atlantic .....	26	1,558,181	22,608	2,288,498
Pennsylvania .....	14	744,565	10,168	855,608
Other <sup>4</sup> .....	12	813,616	12,440	1,432,890
North Central .....	40	1,584,241	21,565	2,418,801
Illinois .....	15	837,008	10,894	1,135,991
Michigan .....	5	102,928	1,606	133,244
Ohio .....	14	446,755	6,660	624,377
Other <sup>5</sup> .....	6	197,550	2,405	525,189
South .....	92	2,862,891	33,773	5,062,336
Alabama .....	10	60,996	706	184,333
Georgia .....	15	36,525	425	241,789
Louisiana .....	6	343,666	4,432	462,049
South Carolina .....	9	12,200	164	165,981
Other <sup>6</sup> .....	52	2,409,504	28,046	4,008,184
West <sup>7</sup> .....	14	717,287	9,375	827,380

1. Gross quantities including spent sulfuric acid fortified in contact units.
2. Includes data for 85 plants operating chamber units; 82 plants operating contact units; and 10 plants operating both types of units.
3. Includes data for plants located as follows: Connecticut 1; Maine 1; Massachusetts 2; Rhode Island 1.
4. Includes data for plants located as follows: New Jersey 9; New York 3.
5. Includes data for plants located as follows: Indiana 3; Missouri 2; Wisconsin 1.
6. Includes data for plants located as follows: Arkansas 1; Delaware 1; Florida 6; Kentucky 1; Maryland 6; Mississippi 3; North Carolina 9; Oklahoma 2; Tennessee 3; Texas 7; Virginia 12; West Virginia 1.
7. Includes data for plants located as follows: Arizona 2; California 8; Colorado 1; Montana 1; Utah 1; Washington 1.

\*Census of Manufactures, Vol. II. Statistics by Industries, p.389.

Mississippi River system and its tributaries, the Ohio and Illinois waterways. This combination of low-cost transportation and production, as long as the supply of Gulf Coast sulfur was ample, precluded the development of alternative sources of sulfur supply.

Consumption of sulfur in Illinois and other states adjacent to the Mississippi-Ohio river system can be approximated from the data on barge shipments on the waterways. This movement for the year 1949 was as follows:

A total of 777,649 tons moved northward on the Mississippi River.

Of this total 232,533 tons was unloaded in the St. Louis and East St. Louis districts, and

339,095 tons was unloaded at points on the Illinois waterway, mainly in the Chicago district.

Consumers on the Ohio River and at Pittsburgh took 199,413 tons and 6,606 tons was shipped beyond St. Louis into the upper Mississippi River area.

Table 3 shows the tonnages of sulfur terminated by railroads in states of the upper Mississippi-Ohio waterway area, for the years 1949 and 1950. The total quantity so reported is somewhat less than the tonnages shipped over the Mississippi, Illinois, and Ohio waterways. These tonnages are presumed to be sulfur originating on river ports and shipped by rail for further destinations in the respective states.

TABLE 3. SULFUR SHIPMENTS TERMINATED ON RAILROADS IN STATES OF THE UPPER MISSISSIPPI-OHIO VALLEY, 1949 AND 1950\*.

States	TONS	
	1949	1950
Illinois .....	113,588	100,033
Indiana .....	37,187	63,932
Iowa .....	22,893	29,689
Michigan .....	61,136	63,478
Minnesota .....	1,004	4,382
Missouri .....	125,609	36,959
Ohio .....	118,409	106,705
Wisconsin .....	70,179	33,207
Total	549,975	438,385

\*Source: Interstate Commerce Commission, Bureau of Transport Economics and Statistics.

## PART II — SOURCES OF SULFUR

## NATIVE SULFUR

Crude native sulfur produced by the Frasch process from salt domes in Texas and Louisiana will continue to be the principal source of sulfur for an indefinite time. The present sulfur problem arises from the fact that demand is exceeding production. The relation of demand to production in recent years is shown in table 4.

TABLE 4. PRODUCTION, MINE SHIPMENTS, AND PRODUCERS' STOCKS, 1947 TO 1950<sup>1</sup>  
(in thousands of long tons)

Year	Production	Shipments			Producers' stocks <sup>3</sup>
		domestic	export	total <sup>2</sup>	
1947	4441	3529	1299	4828	3371
1948	4869	3716	1263	4979	3225
1949	4745	3358	1431	4789	3099
1950	5192	.....	.....	5504	2655
Jan.-Sept. 1951	3964	.....	.....	3760	2754

<sup>1</sup>Bureau of Mines, Mineral Market Report, Nos. 58, 82, 93, 98, and 102.

<sup>2</sup>Mine Shipments.

<sup>3</sup>Producers' stocks at mines, in transit, and in warehouses at end of period.

Table 4 indicates a consumption of sulfur in excess of production in 1949 and 1950 and a decrease in producers' stocks to less than six months' supply, a situation which is described as "dangerously low."

Sulfur is now being produced in the Gulf Coast area of the states of Louisiana and Texas on the following sulfur-producing domes:

- 1) Louisiana  
(Lake Washington)  
Grande Eaille Mine — Plaque Mines Parish
- 2) Texas  
Orchard Dome — Fort Bend County  
Hoskins Mound — Brazoria County  
Clemens Dome — Brazoria County  
Long Point Dome — Fort Bend County  
Boling Dome — Wharton County  
Moss Bluff Dome — Liberty County (New in 1948)

Efforts to sustain sulfur production in the Gulf Coast are being attempted by exploratory activities on salt domes in Louisiana and Texas as follows:

- 1) Louisiana — Bay Ste. Elaine  
     Exploratory wells being drilled  
     Garden Island\*  
     Nash Dome — Texas  
     Venice Dome  
     Starks Dome — Calcasieu Parish
- 2) Texas — Spindletop Dome, Texas — Jefferson County

#### SUPPLEMENTARY SOURCES OF SULFUR

Potential sources of sulfur of varying degrees of practicality are:

1. Pyrite.
2. Sulfides of non-ferrous metals — lead, zinc and copper obtained in smelter gases.
3. Hydrogen sulfide in natural gas.
4. Hydrogen sulfide from oil refinery operations.
5. Sulfur from coal
  - a. Coal "brasses" (iron pyrite) separated from coal at cleaning plants.
  - b. Hydrogen sulfide from by-product coke-oven gases.
  - c. Sulfur dioxide from stack gases of coal-burning power plants.
  - d. Sulfur, as iron pyrite, in washing refuse piles of coal operations.
6. Gypsum and anhydrite.
7. Low-grade sulfur deposits in western states.
8. Reclaimed sulfuric acid.

These alternative sources of sulfur will assume a position of increasing importance. High cost of preparation or conversion of sulfur into marketable forms and high transportation costs of sulfur ores, or sulfur compounds, where transportation to market is necessary, will tend to favor the development of local sources and many production units. This will further result in the development of several types of sources, depending upon the economic situation in a given market area.

#### SULFUR FROM ILLINOIS

An examination of local sources of sulfur for Illinois markets pro-

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\*On August 30, 1951, the Bureau of Mines announced "the discovery reported by the Freeport Sulfur Co., of a large sulfur deposit at the Garden Island Bay dome in the Mississippi delta, which is expected to produce approximately 500,000 long tons annually before the end of 1953."

ceeds from the assumption that higher production costs of sulfur from these sources may be offset by savings in transportation costs from distant sources.

### Coal

Sulfur content in Illinois coal is discussed by Cady<sup>1</sup> and a summary of his findings are reproduced herewith:

#### "SUMMARY OF OBSERVATIONS ON THE QUANTITATIVE OCCURRENCE OF SULFUR AND ITS FORMS"\*

"(1) Total sulfur in Illinois (coals) generally exceeds 3 percent\* and in most places and seams ranges from 4 to 6 percent. In a few local areas the sulfur content of a coal is less than 3 percent, not uncommonly in these areas being less than 2 percent. The countries in which these areas are located and coal beds are as follows:

Jackson County .....	Murphysboro (No. 2) coal
Will County.....	LaSalle (No. 2) coal
Woodford County .....	LaSalle (No. 2) coal
Saline County .....	Harrisburg (No. 5) coal
Vermilion County.....	Springfield (No. 5) (Grape Creek coal)
Eastern Perry, Jefferson, Franklin, and Williamson counties .....	Herrin (No. 6) coal

"(2) Within the limits of variation of each group the amount of total sulfur is very erratic, making it difficult to discover any definite relationships.

"(3) Sulfate sulfur is an unimportant constituent of Illinois coals ( $\frac{1}{4}$ - $\frac{1}{2}$  percent).

"(4) (a) Pyritic Sulfur in coals having a low total sulfur content is necessarily low, not exceeding 2 percent in coals containing 3 percent or less of total sulfur, but within these limits it is variable since it may be as little as 0.25 percent.

"(b) Pyritic sulfur in coals having a total sulfur content exceeding 3 percent varies irregularly to such an extent as to account for a 5 percent variation in the total sulfur content, that is, from 3 to 8 percent.

"(c) Free or discardable pyrite, if included in the analytical results, would rarely increase the average sulfur values more than 2 percent and in most cases not more than 1 percent of the weight of the coal. Coals having a total sulfur content of less than 3 percent probably rarely have an additional discardable sulfur content in the form of pyrite of more than 0.5 percent.

<sup>1</sup>Cady, G. H., Distribution of Sulfur in Illinois Coals and Its Geological Implications. Contributions to the Study of Coal, Illinois Geol. Survey Rept. Inv. 35, 1935.

\*In this summary, percent values refer to weight of the coal on an ash and moisture free basis."

"(5) (a) Organic sulfur, in contrast to total and pyritic sulfur, displays considerable regional regularity and fairly systematic variation from place to place in certain beds. Local areas of low total sulfur are also areas of low organic sulfur.

"(b) Local variation in organic sulfur is rarely more than 1 percent and generally not more than 0.5 percent irrespective of the locality.

"(c) Low organic sulfur content (less than 1 percent) is usually accompanied by low pyritic and total sulfur content; high organic sulfur content is usually accompanied by high pyritic (more than 2 percent) and total sulfur (more than 3 percent) contents.

"(6) The most significant result of this examination of the occurrence of total sulfur and the chemical forms of sulfur is the conclusion that the organic sulfur is the best index of the sulfur content and that the organic sulfur content is regionally consistent for each coal bed."

#### *Coal "Brasses"*

Among the by-product sources of sulfur not now exploited is the pyrite found in coal, referred to as coal "brasses."

Pyrite occurs in bands and nodules in the coal bed, some of which is recoverable from coal in the cleaning process.

Coal cleaned in Illinois and Indiana<sup>2</sup> totaled 38 million tons in 1949 of which 27 million were in Illinois and 11 million in Indiana. The average annual tonnage cleaned in a five-year period 1945-1949, for these two states was 42,807,462 tons.

Assuming one-percent recovery of pyrite from coal processed in cleaning plants, there is on the basis of existing capacity an ultimate possibility of 400,000 tons of pyrite, about 40 percent sulfur.

There are approximately 70 coal-cleaning plants in Illinois and 20 in Indiana, some of which can be equipped to recover pyrite provided there is sufficient incentive to do so. Incentive would include such elements as adequate price, continued demand, and an agreement by the purchaser to take all pyrite produced and offered for sale. The technical problem of using a pyrite contaminated with carbon for the manufacture of sulfuric acid would also need to be solved.

#### *Mine Refuse*

In various coal-mining localities in Illinois, there are large tonnages of mine refuse. "The coal in central Illinois, in the Springfield-Taylorville area, is especially high in sulfur . . . the refuse piles contain about 12 percent sulfur."<sup>3</sup> Investigations for the recovery of sulfur from refuse piles have been undertaken by one coal company. Estimates of the quantity of sulfur in these refuse piles are unavailable.

#### *Coke-Oven Gases*

The quantity of hydrogen sulfide in gases of by-product ovens in the Chicago industrial district in 1949 is estimated at 30,000 tons. This is

<sup>2</sup>Indiana production may be considered with Illinois as part of the potential supply of sulfur from coal.

<sup>3</sup>Wall Street Journal, Chicago edition, February 10, 1951, p. 2.

based on data on sulfur compounds in coke and coke-oven gases reported by Wilson and Wells' and on reports of the Bureau of Mines of coal consumption and gas production in coke ovens. Wilson and Wells report as follows:

"The sulfur in the coal is distributed among the carbonization products, usually in the following approximate proportions:

	Percent
Coke .....	50-65
Gas, as hydrogen sulfide .....	25-30
As carbon disulfide, thiophene, and other organic sulfur compounds .....	1-1.5
Tar and ammonia liquor .....	Balance

The following relationships have been given as rough guides for predicting the sulfur contents of coal gas. The hydrogen sulfide content in grains per 100 cu. ft. equals the percent of sulfur in the coal times 365; and the organic sulfur in grains of sulfur per 100 cu. ft. equals the percent of sulfur in the coal times 18.

"Hydrogen sulfide and other sulfur compounds in the volatile products begin to form in quantity around 250°C. (482°F.), but the reactions which produce them are probably largely completed in the temperature range 500 to 800°C. (932 to 1472°F.). Both the sulfur combined in the coal substance itself and that in the mineral matter of the coal contribute to the formation of volatile sulfur compounds. Organic molecules containing sulfur probably decompose under the influence of heat to form hydrogen sulfide and volatile, organic-sulfur compounds. The mineral matter takes part in a number of reactions which produce volatile sulfur compounds. Thus, when iron pyrite,  $FeS_2$ , is heated in contact with organic matter, hydrogen sulfide is evolved to leave ferrous sulfide,  $FeS$ . The latter, in turn, can react with the carbon of the coal substance to produce carbon disulfide. On heating in contact with organic matter, sulfates in the mineral matter are reduced to sulfides, and these, in turn, can react with more organic matter to form organic-sulfur compounds."

Coal consumed in the manufacture of by-product coke in Illinois and Indiana (principally in the Chicago industrial district) in 1949 was 14,852,295 tons. This coal is obtained mainly from eastern Kentucky, West Virginia, and Virginia and generally is low in sulfur. A sulfur content of 0.8 percent is assumed. This gives a value of 118,818 tons of sulfur in the coal consumed in coke ovens. If 25-30 percent of the sulfur, as stated by Wilson and Wells, appears as hydrogen sulfide in gas, this gives a quantity of 29,700 to 35,600 tons of hydrogen sulfide.

When sulfur content is calculated on the basis of grains per 100 cubic feet, according to the formula of Wilson and Wells, on a basis of 144,268,392,000 cubic feet of gas produced by coke ovens in 1949,<sup>5</sup> using

<sup>4</sup>Wilson, Philip J., and Wells, Joseph H., *Coal, Coke, and Coal Chemicals*, McGraw-Hill and Co., 1950, pp. 188-189.

<sup>5</sup>Bureau of Mines, *Minerals Yearbook*, 1949, Chapter on Coke and Coal Chemicals.



coal of an assumed 0.8 percent sulfur content, the potential supply is calculated at 30,026 tons. The equation based upon the formula is as follows:

$$\text{Sulfur (in tons)} = \frac{365 \times 0.8 \times 144,268,392,000}{437.5 \times 16 \times 100 \times 2000} = 30,026$$

Several processes have been designed to remove hydrogen sulfide from coke-oven gas with or without the recovery of sulfur. These processes are reviewed in several recent articles in chemical literature:

- Organic Sulfur Compounds in Water Gas and Coke Oven Gas: W. A. Kemper and E. W. Guernsey, Amer. Gas Assoc. Proceedings, Vol. 1942, pp. 364-374.
- Coking Dividend; Ford Accumulating Pile of Sulphur Extracted from Coke Oven Gas: Business Week, Dec. 18, 1943, p. 74.
- Ford Starts Sulphur Extraction Plant to Purify Coke Oven Gas: Iron Age, Vol. 152, Dec. 16, 1943, p. 72.
- Hydrogen Sulphide Removal; The Recovery of Sulphur from Commercial Gases: D. D. Howat, The Chemical Age, Vol. 49, July 24-31, 1943, pp. 75-78, 99-105.
- Sulphur Removal and Recovery from Coke Oven Gas: Ford River Rouge Plant Uses Thylox System: N. G. Farquhar, Chemical and Metallurgical Engineering, vol. 51, pp. 94-96, July 1944.
- Coke Oven Gas (Sulfur Recovery): N. G. Farquhar, Iron and Steel, Vol. 18, No. 3, pp. 84-85, March 1945.
- Sulphuric Acid from Coke-Oven Gas: W. A. Leech, Jr., and F. D. Schreiber, Iron and Steel Engineer, Vol. 23, No. 12, pp. 93-101, Dec. 1946.
- Sulfur ( $H_2S$ ) from Industrial Gases: Reed, Robert M., and Hpdgraff, Norman C. Processes in Removal of Hydrogen Sulfide from Industrial Gases. Paper presented before the 117th meeting of the American Chemical Society, Houston, Texas, March 17, 1950.
- Johnstone, H. F., Read, H. J., and Blankmeyer, H. C., Industrial and Engineering Chemistry, vol. 30, p. 101, 1938.
- Johnstone, H. F., Industrial and Engineering Chemistry, vol. 29, p. 1396, 1937.

### *Stack Gases of Coal-Burning Power Plants*

Sulfur dioxide in spent gases of coal-burning power plants has been considered as a source of sulfur. A comprehensive study of the recovery of sulfur as sulfur dioxide has been made at the University of Illinois.\* The recoverable sulfur could, if fully recovered, more than meet the sulfur dioxide and sulfuric acid requirements of Illinois and adjacent states.

The quantity of coal used in public utility power plants in Illinois and Indiana in 1950 was as follows:

In Illinois .....	12,030,578 tons
In Indiana .....	6,416,858 tons
Total .....	18,447,436 tons

The sulfur content of coal used by public utilities varies in percentages in a range of about 1 percent to 3 percent. With an increasing tendency to wash coal, the sulfur percentage will also tend to decrease. The quan-

\*Johnstone, H. Fraser, and Singh, A. D., The Recovery of Sulphur Dioxide from Dilute Waste Gases by Chemical Regeneration of the Absorbent. Bull. Series No. 324, University of Illinois, Engineering Experiment Station, 1940.

tity of sulfur, therefore, entering into the stokers of power plants may vary from 180,000 tons as an approximate minimum to 550,000 tons as a likely maximum. Seventy to 90 percent of the sulfur in the coal enters into the stack gases. The following excerpt is from Johnstone and Singh,

*The Recovery of Sulphur Dioxide, etc.:*

"Flue gases from high sulphur coals contain from 0.2 to 0.5 percent  $\text{SO}_2$  by volume. At one plant, which burns coal containing 4.45 percent sulphur on stokers, the average  $\text{SO}_2$  content of the gas is 0.279 percent for 10.7 percent  $\text{CO}_2$ . The sulphur trioxide content is 0.0082 percent. At another plant, burning the same coal in the powdered form, the average  $\text{SO}_2$  content is 0.413 percent when the  $\text{CO}_2$  is 13.6 and the  $\text{SO}_3$  is 0.0032 percent. These values indicate that 70 percent of the sulphur enters the gas when the coal is fired on a stoker and this is increased to 90 percent when it is fired as pulverized fuel. The amount of sulphur converted to trioxide, or sulphuric acid vapor, is only about two percent of the total gaseous sulphur . . .

"Gases containing more than two percent sulphur dioxide have long been treated by direct conversion to sulphuric acid either by the chamber process or by the contact process. Dilute gases, however, are costly to treat, but are often sources of nuisance.

"The problem, therefore, requires the development of a process for the treatment of a very large quantity of hot dust-laden gases to remove a dilute constituent, amounting to several hundred tons per day, without undue interference with the operation of the plant, or excessive costs of operation."

The investigations of Johnstone and Singh also showed that the removal efficiency of  $\text{SO}_2$  from flue gases varied from 81.8 to 98.2 percent. "Over the twelve-hour test period, during which 650,000 cubic feet of gas were scrubbed, the absorption averaged 90.5 percent, and the residual  $\text{SO}_2$  was 64 parts per million."<sup>7</sup>

Johnstone and Singh found that about 90 percent of sulfur in the coal enters the flue gases. Since 90 percent of the above is recoverable as sulfur, it means that, for each 1 percent of sulfur in the coal, 0.8 percent is ultimately recoverable as sulfur dioxide. For the public utility power plants in Illinois and Indiana this would, in 1950 for example, be equal to 0.8 times the average percentage of sulfur in the 18.5 million tons of coal used each year.<sup>8</sup>

In the summary and conclusion of this investigation Johnstone and Singh state, "In this bulletin a new process for recovery of sulfur dioxide from dilute waste gases has been described. A thorough investigation in the laboratory and pilot plant has shown that the process is workable in every respect."

The investigation included a detailed calculation of equipment costs for a sulfur dioxide recovery plant. Although this was made for cost

<sup>7</sup>Johnstone, H. F. and Singh, A. D., *Op. cit.*

<sup>8</sup>It should be pointed out that it is possible that not all public utility power plants could install a recovery process. Also, power plants of manufacturing industries are not included in the above calculations, some of which possibly could make use of the process.

conditions as they existed in 1939, the basis of the calculations, as prepared in the report, can be used to calculate costs under present conditions. The economic position of sulfur from flue gas under existing market conditions in the sulfur industry is determinable from this report.

#### Refinery Gases

Sulfur is being recovered from hydrogen sulfide present in refinery gases. A plant for the recovery of elemental sulfur has been erected near Long Beach, California, to process hydrogen sulfide extracted from sour gas in adjacent refineries. The primary reason for the erection of this plant was the growing smog nuisance in the Los Angeles basin area to which the refineries were accused of contributing. The plant is reported to be recovering 70 tons of sulfur per day.<sup>9</sup> The process used is similar to the Girbitol process also used in the recovery of hydrogen sulfide from sour natural gas.

The reaction in this process is as follows:



Other projects for the recovery of sulfur from refinery operations, completed or in the projected stage, are the Eagle Point, N. J., refinery of the Texas Company, the Sinclair Refining Co., at its Wood River refinery; the Standard Oil Company (Ind.) is building a 100-ton plant at Whiting, Indiana. Refineries in Wyoming and Montana produce considerable hydrogen sulfide and could process this to sulfur, if a local market developed.<sup>10</sup>

The recovery of sulfur in substantial quantities by oil refineries in the Illinois-Indiana area will depend on the sulfur content of the crude oils processed in this area and the projected price of sulfur after controls are removed.

In general, crude oil shipped to refineries in Illinois and Indiana is low in sulfur content, although some high-sulfur crudes from west Texas and Wyoming are processed in Illinois refineries. In a detailed report of sulfur content of United States oil fields, Smith and Blade<sup>11</sup> classify nine major producing areas in the United States by sulfur content. For Mid-Continent and Illinois fields they give the following data for the year 1946:

Field	Average production B/D
Sulfur content 0 — 0.25 percent	
Mid Continent .....	210,254
Ill., Ind., W. Ky. ....	14,855

<sup>9</sup>U. S. Petroleum Industry to Become Net Sulfur Producer, World Petroleum, Annual Refinery Issue, 1951, p. 65.

<sup>10</sup>*Op. cit.*, p. 67.

<sup>11</sup>Smith, H. M., and Blade, O. C., Trends in Supply of High-Sulfur Crude Oils in the United States, Oil and Gas Jour., vol. 46, no. 30, Nov. 29, 1947, pp. 73-78.

Field	Average production B/D
Sulfur content 0.26 – 0.50 percent	
Mid Continent .....	571,994
Ill., Ind., W. Ky. ....	21,500
Sulfur content 0.5 – 1.0 percent	
Mid Continent .....	146,332
Sulfur content 1.0 – 2.0 percent	
Mid Continent .....	33,909
Sulfur content 2.0 + percent	
Mid Continent .....	77,915

About 280 million barrels of crude oil is processed annually by refineries in Illinois and Indiana, located mainly in the Chicago area, the Wood River, Illinois, area and southeastern Illinois. If it is assumed that a barrel of oil weighs 300 pounds and the average content of sulfur in crude oil processed in Illinois and Indiana is estimated at 0.25 percent, the total sulfur content of oil processed in Illinois would be approximately 105,000 tons. Only a part of this appears as hydrogen sulfide in the refining process and is recoverable.

#### SULFUR SUPPLIES OUTSIDE THE ILLINOIS MARKET AREA

The preceding section covers sources of sulfur from raw materials located in the Illinois market area or shipped into this area for processing. Competition for the Illinois market from sources outside the area must also be taken into account. These potential competitors are hydrogen sulfide in natural gas, sulfur dioxide in smelter gases, pyrite, low-grade sulfur deposits in the Western states, and, remotely, anhydrites.

##### *Natural Gas*

The recovery of sulfur from the hydrogen sulfide in natural gas from some fields in Western states has become of interest as a commercial by-product. Hydrogen sulfide is recovered from natural gas as elemental sulfur by the Girbitol process. This process has been described in detail in the technical literature and is briefly described below:<sup>12</sup>

An absorbent solution is passed downward through a bubble tray absorber countercurrent to the gas. The rich absorbent is heated by exchange and stripped with steam in a second column. The lean absorbent is then cooled and recycled. The absorbent may be an aqueous solution of monoethanolamine, diethanolamine, or a mixture of one or both with diethylene glycol.

The second step in sulfur recovery consists of reacting two molecules of H<sub>2</sub>S with one molecule of oxygen. The process employed was de-

<sup>12</sup>World Petroleum Twenty-first Annual Refinery Issue, 1951. p. 67.

veloped by Claus in Germany about 1880. Improvements were made in the process by I. G. Farben industries during the Second World War. In the modified process, part of the acid gas is burned with controlled air to produce sulfur dioxide and by-product steam. Combustion products are mixed with the remaining  $H_2S$  concentrate and passed over a bauxite catalyst. Reaction of the hydrogen sulfide and sulfur dioxide produces sulfur vapor and steam. The sulfur is condensed by direct contact with cooled liquid sulfur.

Sulfur-bearing natural gas is produced mainly in the Western states.<sup>24</sup> Recovery plants and their locations are:

Texas Gulf Sulphur and Pure Oil Co., Worland, Wyoming

Phillips Chemical Company, near Goldsmith, Texas, in Permian Basin fields

Southern Acid and Sulfur Co., McKamie field, Arkansas

Odessa National Gasoline Company and Sid Richardson, Carlson Co., Odessa, Texas

Elk Basin plant, Montana-Wyoming

Sulfur from hydrogen sulfide in natural gas is produced as elemental sulfur and is therefore directly competitive with elemental sulfur shipped in from the Texas and Louisiana Gulf Coast. In elemental form, sulfur can be transported at a low cost and becomes competitive over a wide market area.

Table 5 gives a list of states in which sulfur from natural gas recovery plants will find its principal market. Apparent consumption of elemental sulfur in 1950 in these states was approximately 55,000 tons. An additional 140,000 tons is consumed in Pacific Coast states. Sulfur recovered from natural and refinery gases in these market areas is shown by the data collected by the Bureau of Mines to be more than 150,000 tons. This, together with anticipated development, may be sufficient to satisfy the sulfur demands of the mountain states and Pacific Coast area. An equivalent tonnage of sulfur from Texas and Louisiana will be released to Midwest and Atlantic Seaboard markets.

#### *Smelter gases*

Each year, large quantities of sulfur dioxide are evolved in the smelting of non-ferrous sulfide ores. The principal source of by-product sulfuric acid at present is zinc smelters, and secondly, copper and lead smelters. Production of by-product sulfuric acid from zinc and copper smelters in recent years is shown in table 6.

Because the most important source of by-product sulfuric acid is from zinc smelters, their potential contribution must be considered. Zinc is recovered from several ores of which zinc blende is the most important and also the only sulfur-bearing zinc ore. Zinc blende contains 67 percent zinc and 33 percent sulfur. This is the principal ore in the Tri-State district, in the Appalachian zinc belt, in the Couer d'Alene district, and other districts in the mountain states. In complex

<sup>24</sup>There is some production of sour gas in Arkansas.

TABLE 5. APPARENT CONSUMPTION OF ELEMENTAL SULFUR  
IN THE SOUR GAS AREA, 1949 AND 1950\*  
(tons)

	1949	1950
North Dakota .....	174	153
South Dakota .....	138	20
Nebraska .....	1,027	1,949
Kansas .....	1,015	11,664
	<hr/>	<hr/>
	2,354	13,786
Montana .....	308	517
Idaho .....	726	1,283
Wyoming .....	1,699	1,728
Colorado .....	5,479	6,343
New Mexico .....	381	181
Arizona .....	24,579	30,240
Utah .....	1,041	612
Nevada .....	181	110
	<hr/>	<hr/>
	34,394	41,014

\*Based upon tonnages of sulfur terminated by railroads in each of the states. Statement No. Q-550 (SCS). 1949 and 1950, Interstate Commerce Commission.

ores, galena, the principal lead ore, with a 14 percent sulfur content, is frequently associated with zinc ores. In addition to the sulfides of non-ferrous metals, pyrite may also be associated in the ore body. Altogether, a considerable quantity of sulfur is present in principal non-ferrous ores. In the annual output of 700,000 tons<sup>14</sup> of zinc from zinc blende, there is a potential supply of 350,000 tons of sulfur, as contrasted with 199,000 tons actually recovered in 1949. Treatment of lead and copper ores and associated pyrite may raise this somewhat. Nevertheless, expansion of output over 241,000 tons from all non-ferrous sources would be not more than double present output.

The possible contribution of smelter-produced sulfur to Midwestern markets, apart from the limited additional quantity producible, is also circumscribed by the demands of the local market. Sulfuric acid made

<sup>14</sup>Out of a processing of 814,000 tons of domestic and imported ore, a conservative figure of 700,000 tons from zinc blende has been assumed.

TABLE 6. BY-PRODUCT SULFURIC ACID (BASIS 100 PERCENT)  
FROM SMELTING OF NON-FERROUS ORES.\*

	from zinc plants	from copper plants	Total
1941	522,090	188,200	710,290
1942	540,000	206,000	746,000
1943	685,000	271,000	956,000
1944	653,000	249,500	902,500
1945	610,938	231,697	842,635
1946	544,529	171,687	716,216
1947	598,703	126,494	725,197
1948	529,478	111,967	641,445
1949	476,932	96,344	573,276
1950	609,571	131,342	740,913

\*Sources: Bureau of Mines, Minerals Yearbooks.

from by-product gases appears from the statistics to be insufficient for the local market. In addition to the production of 552,190 tons (1945-49 average) of sulfuric acid obtained from zinc-blende roasting plants, 205,255 tons (1945-49 average) were made from native sulfur.

For the Illinois sulfur market, the contribution from zinc smelters may be limited to output from Illinois zinc plants. In 1949 this was 87,000 tons of stab zinc with a theoretical maximum of 43,500 tons of sulfur.

#### *Pyrite*

Pyrite ( $\text{FeS}_2$ ) is frequently considered as the most likely alternative to elemental sulfur as a source of supply for the manufacture of sulfuric acid. Before World War I, 50 percent of sulfuric acid was made from imported Spanish pyrite, 8 percent from imported Canadian pyrite, 16 percent from domestic pyrite including coal "brasses." Brimstone supplied only 2.6 percent and the remainder came from smelter gases. Since then brimstone has displaced pyrites from all sources. Pyrites, in order to compete in the acid market, must have local advantages such as low shipping costs of either the raw material or the acid product.

In the event of a shortage of elemental sulfur, pyrites must again be considered as a source of supply. The possible sources of pyrite are:

1. Pyrite deposits in the United States.
2. Pyrite associated with copper, lead, and zinc ores and in the tailings of mining operations and as pillars and walls in mine workings.
3. Imports of pyrite from Spain.
4. Pyrite deposits of Canada.

For the sulfur market in Illinois some of the above sources must be eliminated as impracticable.

#### *Imported pyrite.*

Pyrite has been imported into the United States in considerable quantities from Canada and Spain. The Spanish imports supplied the sulfuric acid plants along the Atlantic Seaboard mainly through the ports of Philadelphia and Baltimore. Pyrite was carried as ballast at low rates from the port of Huelva, Spain. Nevertheless, Spanish imports were unable to compete with brimstone from the Gulf Coast salt domes. Imports, which at one time exceeded 300,000 tons annually, declined to less than 13,000 tons in 1949. Spanish imports have ceased to be a factor in the American sulfuric acid industry.

Imports of pyrite from Canada have assumed considerable proportions. Since World War II practically all the Canadian shipments have entered this country through the Buffalo customs district.

Pyrite is produced in Canada as a by-product in the treatment of copper-pyrite ores at Waite-Amulet and Noranda mines in Quebec and at Britannia mine in British Columbia. Both Noranda and Waite-Amulet recover pyrite and ship it to Canadian and American markets (table 7).

It is somewhat difficult to evaluate the possible contribution of Canada to the sulfur requirements of the Illinois market area. As shown in the above table, pyrite is available for export, but at the same time, Canada was an importer of sulfur from the United States. A balance sheet of sulfur production and consumption in Canada for a recent year (1949) is as follows:<sup>16</sup>

Production (in tons)	as sulfur
pyrite .....	117,581
smelter gas .....	144,290
Total .....	261,871
Consumption	
pyrite burned .....	34,600
smelter gas .....	144,300
imported elemental sulfur .....	327,800
Total .....	506,700

<sup>16</sup>Bonham, W. M., Canada's Sulfur Supplies, Canadian Mining Jour. vol. 72, Jan. 1951, pp. 47-50.



TABLE 7. IMPORTS OF PYRITE FROM CANADA, THROUGH THE BUFFALO CUSTOMS DISTRICT, AND TOTAL IMPORTS (short tons)

Year	Imports through Buffalo customs district	Total imports
1934	49	21,650
1935	105	11,050
1936	157	61,650
1937	655	23,000
1938	5,745	33,580
1939	24,600	157,600
1940	89,650	90,800
1941	254,000	273,500
1942	252,000	317,500
1943	178,000	220,000
1944	151,000	186,000
1945	143,100	153,600
1946	136,100	136,200
1947	41,000	95,200
1948	74,200	84,200
1949	119,500	121,000
1950	.....	.....

The local demand upon Canadian sources of sulfur is expected to increase in the future because (a) shipments of elemental sulfur from the United States have been curtailed, and (b) Canadian industry has expanded, accompanied by increased sulfur requirements.

Major Canadian expansion of sulfur supply is expected by recovery of sulfur now going to waste in smelter gases of nickel, copper, and zinc

smelters. Potential recovery from these sources is estimated at a total of 1,520,000 tons annually of sulfur from the following sources:

	Tons
International Nickel Company .....	1,000,000
Noranda .....	355,000
Flin Flon .....	165,000
Total .....	1,520,000

Sulfur from these sources would be recovered as elemental sulfur at Noranda and as sulfur dioxide at International Nickel. The latter would be distributed to markets in liquid form in tank cars. Unless these sources of sulfur are developed, increases in Canadian sulfur requirements in the face of decreasing imports from the United States will have to be met by roasting pyrite ores.<sup>16</sup>

#### *Domestic pyrite.*

Domestic pyrite does not appear to be promising as a source of sulfur for requirements of the Illinois market area. With the exception of zinc and lead mining operations in Missouri, the Tri-State district, and the Illinois-Wisconsin zinc district, the major non-ferrous metal operations are remote from Midwest markets; and freight rates, either for pyrite or liquefied sulfur dioxide, would be too high to enable these ores to compete with local sources of sulfur supply.

There are four principal deposits of pyrite ores, of 10 million long tons, or mine reserve, in Maine, Virginia, Tennessee, and Arizona. Deposits of less than 10 million tons are located in New York, Georgia, Alabama, California, and Missouri. The last may be worthy of examination as a possible source of sulfur for St. Louis requirements.

As in the case of pyrite associated with non-ferrous metal ores, a high transportation cost is involved in getting this ore into upper Mississippi markets.

#### SUMMARY

The discovery of a sulfur-bearing salt dome in Garden Bay, Louisiana, does not change the need of establishing a sulfur-producing industry on a broader basis.

There is an abundance of sulfur potentially available although a higher price will be needed to exploit these resources.

The Illinois sulfur market area produces (and consumes) about 24 percent of the nation's sulfuric acid. Sulfur (as brimstone) has been available at low transportation costs over the Mississippi, Illinois, and Ohio waterways.

A decline in the supply of elemental sulfur will necessitate the development of supplemental and alternative sources, such as sour gases,

<sup>16</sup>A large deposit of pyrite is reported at Gondreau, northeast of Lake Superior, about ½ mile from the port of Michipicoten.

smelter gases, stack gas, coke-oven gases, pyrite deposits both primary and associated with non-ferrous ore deposits, and coal "brasses." Within the Illinois sulfur market area or brought into it for processing, there is a ready sulfur supply in the form of coal "brasses," sulfur dioxide in stack gases, hydrogen sulfide in refinery gases and coke-oven gases. There are ample supplies of sulfur among these several sources to supply all the requirements of the Illinois sulfur market if the need should ever arise.

For meeting the supplemental needs arising out of a deficiency of native sulfur supply, a process of sifting will be necessary to find the most economical source of supply from among the several sources potentially available.

Possible producers of coal "brasses" to provide a sulfur supply must evaluate the possible competitive position of sulfur from stack gases, oil-refinery gases, and imported pyrites.

\* \* \*

Chairman Morris: Thank you, Dr. Voskuil. Are there any questions you would care to ask Dr. Voskuil?

Gentlemen, it has been a pleasure to be Chairman of this session and I want to thank you for your interest in this session. I will now turn the meeting over to Mr. Schonthal.

Mr. Schonthal: The only thing I would like to suggest is that anybody who expects to attend the dinner tonight should get his ticket without further delay because we are going to have a big crowd. We have a very good speaker. We have been a little delayed but I think we will still be able to set the dinner for 6:30 sharp. We will call this meeting adjourned. Thank you very much.

(Adjourned at 4:30 P.M.)



